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Service life prediction of AP/Al/HTPB solid rocket propellant with consideration of softening aging behavior

Walid M. ADEL, Guozhu LIANG *

School of Astronautics, Beihang University, Beijing 100083, China

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Abstract The aging behavior of softening composite solid propellant was investigated by measuring its mechanical and ballistic prosperities during prolonged storage at elevated and room temperatures. Accelerated aging was conducted at 65 °C for 231 days while the normal aging was performed at 25 ± 3 °C and relative humidity less than 50% for 8 years. The mechanical properties were obtained from uniaxial tensile tests for the aged propellant specimens while the ballistic properties were determined from static firing tests of subscale motors aged for 112 days at 65 °C. The mechanical results show that the maximum tensile strength and Young's modulus initially increase and subsequently decrease with increasing aging time, while the maximum tensile strain generally increases with increasing aging time. The ballistic properties like burning rate show a small change which cannot affect the ballistic performance. The experimental results show that the changes in the mechanical properties are significant during the aging period, but the burning rate does not undergo significant changes. From this study, it is observed that the propellant ages through a combination of reactions like post-cure, oxidative cross-linking, chain scission, and hydrolysis. The chain scission and the hydrolysis effect are the most significant process, which makes the propellant soft and extendible. The observed aging mechanism has been modeled using an exponential function with two terms which can describe the complex behavior of the aging. By applying Arrhenius equation, the activation energy values were obtained based on the propellant mechanical properties. The shelf life of this propellant formulation at 25 °C is predicted to be 13 years using the modulus as failure criteria and control parameter.

1. Introduction

Aging is defined as the deterioration of the materials during storage and of all the components in a Solid Rocket Motor (SRM), the material more susceptible to changes over time is the propellant itself, which is the major factor to determine

* Corresponding author.
E-mail address: lgz@buaa.edu.cn (G. LIANG).
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the service life of a rocket motor. Composite solid propellants consist of solid fillers embedded in a rubbery polymeric matrix and the aging of this propellant is very complex due to a combination of the damage caused by physical, chemical, and mechanical processes. These three processes may have an additive or subtractive effect according to the environmental and mechanical loads.

Generally, the longtime equivalent aging properties of the solid propellants were studied using the short time thermal to accelerate aging results, to investigate the aging kinetics and mechanisms,[1,2] to predict the mechanical and ballistic properties of propellant aging,[3,4] to predict the propellant service life,[5] and to find the correlation between the thermal accelerated aging and the real world storage aging of Hydroxyl-Terminated PolyButadiene (HTPB) propellant.[6]

Many works have been carried out to evaluate and characterize the aging behavior of the HTPB solid propellant with the premise that the main aging mechanism is the oxidative cross-linking through the double bonds of polybutadiene,[7–10] and the aging behavior is observed with respect to the kinetic model proposed by Layton's formula which is the most common kinetic model used to describe the results of mechanical aging of propellant.[11,12]

$$P(t) = P_0 + k\ln(t/t_0) \tag{1}$$

where $P(t)$ is the property in specific aging time, P_0 is the unaged property at the end of curing (initial property), k is the aging rate constant, t is the aging time, and t_0 is the time at the end of curing. The rate of change usually can be found by using Arrhenius equation.[13]

$$k = A\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where A is the pre-exponential Arrhenius constant, R is the universal gas constant ($R = 8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$), E_a is the activation energy ($\mathrm{kJ\cdot mol^{-1}}$), and T is the absolute temperature.

Few studies of composite solid propellant aging have shown that when aziridine compounds are present in the formulation as curing,[14] or bonding agent,[15] an initial softening of propellant is observed. The reasons for this behavior were attributed to the cleavage of the polymeric binder at the P–N bond contained in aziridine compounds, due to moisture hydrolysis. Yamamoto et al.[15] suggested a fitting of this initial degradation of tensile strength by a first-order kinetic model as shown in Eq. (3) because Layton's model Eq. (1) cannot simulate this behavior.

$$\ln P = \ln P_0 + k(t - t_0) \tag{3}$$

One of the previous studies has shown evidence of two reactions involved in the overall aging behavior (oxidative hardening and hydrolysis). The propellant studied was a typical polybutadiene formulation using an epoxy/amine bonding agent system. Stress and Young's modulus initially increase with age, and then when the hydrolysis catches up, both properties begin to decrease. This aging behavior has been modeled using a parallel process kinetic model,[16]

$$P(t) = FP_0\frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] + P_0\exp(-k_2 t) \tag{4}$$

where F is a proportionality constant, and k_1, k_2 are rate constants. This model assumes two competing first-order reactions which are the oxidative hardening and the hydrolysis. However, the dominant aging mechanisms affecting propellant behavior due to the chemical and physical process, which normally occur simultaneously, are continued post-curing, oxidative cross-linking, migration of volatile chemicals (e.g. loss of plasticizer, curing agent, hydrolysis, and polymer chain scission).[17–21]

The service life of solid rocket motors can be limited by several causes, for example, the deterioration of material mechanical properties, and changes in ballistic characteristics. Akbas et al.[22] tested aged HTPB propellant at various temperatures between 50 and 100 °C, and the useful life was predicted to be approximately 7 years from the extrapolation to the normal storage temperature of 20 °C based on Arrhenius model. They took the percentage of the elongation at break point for the lifetime prediction. Du et al.[23] estimated the storage life of HTPB propellant as 13.19 years based on linear and logarithmic models by using the accelerated aging data at high temperature and taking the elongation rate as failure criteria. Shekhar[24] predicted the shelf life at 27 °C from data of shelf life at 60 °C as 20 years based on Arrhenius and Berthelot equations, and he took the elongation as the fastest degradation parameter for AP/Al/HTPB solid propellant. Several researchers have predicted the shelf life of HTPB propellants with normal aging mechanism, and generally the shelf life of this type of propellants ranges from 12 to 25 years under normal storage conditions.[25]

Actually, the effect of hydrolysis is not completely understood, and few studies[16,26] have been done on the softening aging behavior of composite solid propellant based on HTPB while no study was previously found to predict the service life of AP/Al/HTPB propellant with this aging mechanism. Therefore, in the present study, we are investigating the softening behavior of the proposed composite solid propellant during the normal and accelerated aging in order to understand the aging mechanism. Also, we are studying the effect of this behavior on ballistic and mechanical properties of the solid propellant, and we choose the mechanical properties as aging parameters because those can be easily measured, sensitive to degradation, and most critical from the structural integrity viewpoint. We built a new mathematical kinetic aging model which can describe the complexity of the aging mechanism based on the mechanical properties only. Finally, the shelf life prediction under the normal storage condition is calculated.

2. Experimental methodology

2.1. Propellant preparation

The solid propellant used in this research is heterogeneous propellant which consists of solid oxidizer particles Ammonium Perchlorate (AP) 67%, metallic fuel particle Aluminum (Al) powder 18%, dispersing in HTPB polymeric binder matrix with a bonding agent based on aziridine compound and isocyanate curing agent, and other ingredients like plasticizer, burning rate modifier, and antioxidant forming the rest percentage. Curing was performed at 60 °C for 10 days. For the uniaxial tensile test, the specimens were produced according to Joint Army-Navy-NASA-Air Force (JANNAF) Propulsion

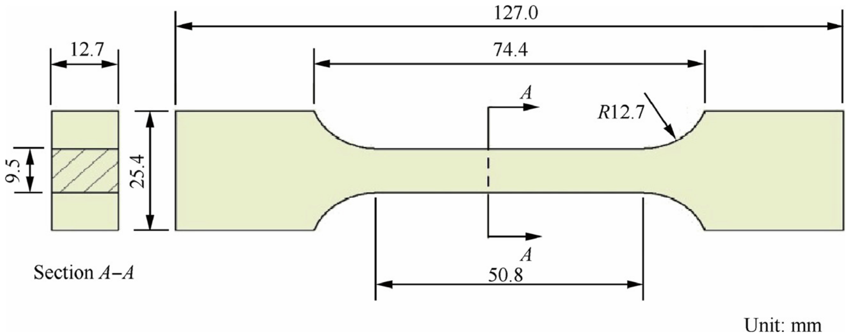

Fig. 1 Standard dimensions of the uniaxial tensile specimen.[27]

Committee standard, and the dimensions of the test specimens are illustrated in Fig. 1.[27]

For the ballistic tests, ten subscale solid rocket motors were produced with circular central port solid propellant grains, according to the dimensions shown in Fig. 2. In order to ensure the safety of the propellant grains in the final firing test, a nondestructive test of the propellants is an essential step. The propellants were scanned using X-ray radiography, which showed the inside homogeneity of the grain and the possibility of any trapped air bubble in the grain body.

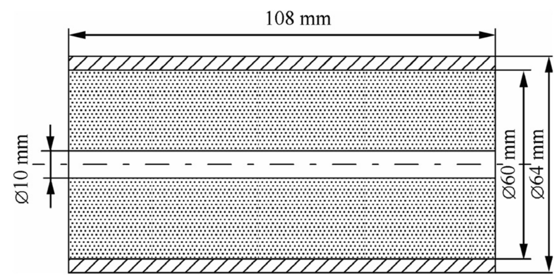

Fig. 2 Schematic diagram of circular perforated grain.

2.2. Aging program

For measuring the mechanical properties, specimens of the propellant from a full-scale production batch wrapped in aluminum foil were aged at a temperature of 65 °C for 231 days (33 weeks) in an explosive-proof forced ventilation oven without humidity control and under atmospheric pressure. Note that temperatures above 70 °C were not attempted as too high values might activate mechanisms which are not present under normal conditions.[3] Specimens were drawn every two weeks and conditioned in desiccators for one day at 30% Relative Humidity (RH) before the tensile test. A normal aging was accomplished at room temperature of 25 ± 3 °C. Some sheets of propellant blocks were cut over 2, 5, 7 and 8 years (417 weeks) after production. The HTPB solid propellants are easy to obtain moisture, so after they were machined, all the normal aging specimens were kept in the oven at 50 °C over 24 h to remove the moisture and residual stresses.[20]

For the ballistic performance tests, 8 subscale motors were aged in an explosive-proof oven at temperature 65 °C for 112 days (16 weeks), which is less than the mechanical one due to the available number of the subscale motors. At every 4 weeks, two motors were withdrawn and conditioned in an external temperature chamber at 21 °C for 24 h before the ballistic test.

2.3. Experimental tests

For the aged propellant specimens, the uniaxial tensile experiments were performed on a computer-controlled universal test machine Zwick Z050 at an ambient temperature of 20 °C with a crosshead speed of 50 mm/min. Therefore, 21 experimental cases were performed in the whole aging procedure, and every experimental test was carried out on three specimens to ensure the repeatability of the measured data, which were averaged to obtain the mean values of Young's modulus E, the maximum tensile strength σ_{max}, and the maximum strain ε_{max} at maximum tensile strength. Also, the Shore-hardness A was measured in specimens with 12.7 mm thickness by using Zwick Shore-hardness tester.

For the ballistic tests, the aged solid propellant rocket motors were placed inside the static test stand for thepressure measurement. All the pressure-time curves obtained from the static firing tests were processed for analysis and calculation of the ballistic parameters, for example, average pressure, burning rate, and burning time. The mechanical, physical, and ballistic properties of the fresh solid propellant after curing are listed in Table 1. The other mechanical properties can be found in Refs.[28,29]

Table 1 Initial properties of composite solid propellant used in this study.

Young's Modulus (MPa)	Maximum Stress (MPa)	Maximum Strain (%)	Shore A	Density ($kg\cdot m^{-3}$)	Average pressure (Bar*)	Burning rate ($mm\cdot s^{-1}$)
3.40	0.724	34.5	60	1760	64.04	14.35

*1 Bar = 100000 Pa.

3. Results and discussion

3.1. Tensile stress-strain behavior

As a result of uniaxial tensile tests, the graph of the stress-strain curves of natural aging propellant specimens is obtained as shown in Fig. 3. Fig. 4 presents the plots of the variation of Young's modulus, maximum tensile strength, maximum tensile strain, and the Shore-hardness, versus the normal and accelerated aging time. The results show that changes that occur during aging clearly, of $\sigma_{\max}$, E, and Shore A, initially increase with normal aging in the first 2 years (104 weeks) and with accelerated aging in the first 3 weeks, while $\varepsilon_{\max}$ initially decreases under the same aging conditions. Subsequently, $\sigma_{\max}$, E, and Shore A start to decrease gradually with normal aging time after 2 years, and with accelerated aging time after 3 weeks, while $\varepsilon_{\max}$ starts to increase under the same aging conditions. The differences between the values of the mechanical properties at the end of curing and at the end of aging time in both conditions are listed in Table 2 as a percentage, and also this table shows that the behavior of this difference increases or decreases according to the initial values. The mechanical properties are strongly influenced by the aging temperature and Table 2 shows that the rate of aging changes slowly at the normal aging temperature while it changes rapidly in the accelerated aging at high temperature.

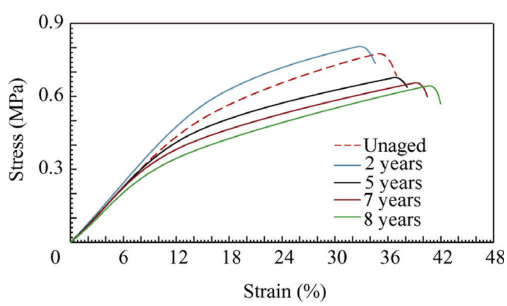

Fig. 3 Tensile responses of normal aged solid propellant specimens.

Table 2 Typical changes in propellant mechanical properties due to aging over life.

Mechanical property	Normal aging (%)		Accelerated aging (%)	
	2 years	8 years	3 weeks	33 weeks
$\sigma_{\max}$	4.0	−19.0	19.0	−38.0
E	6.0	−16.0	24.5	−50.0
Shore A	3.5	−7.0	16.5	−26.0
$\varepsilon_{\max}$	−6.0	17.0	−9.0	84.0

However, in our case, the effect of aging on the mechanical properties was noticed through a softening of the propellant, with a decrease in stiffness, which showed lower values of tensile strength, modulus, and hardness, followed by higher values of elongation. This is an unusual result of HTPB solid propellant aging, and generally, during the aging of this kind of propellant $\sigma_{\max}$, E and Shore A increase while $\varepsilon_{\max}$ decreases with the aging time.[30–33] In order to demonstrate and present the difference between the normal aging behavior of HTPB solid propellant and the HTPB propellant used in this study, we select reference data for accelerated aging solid propellant based on HTPB, which aged also at 65 °C for 20 weeks,[34] to compare these data with our results under the same aging conditions. As illustrated in Fig. 5, the comparison of the mechanical properties of the reference data which represent the normal aging behavior of HTPB solid propellant and the formulated solid propellant used in this work which represent the softening aging behavior of the solid propellant is shown.

Now, it is clear that there is a big difference in aging behavior between the selected (reference) propellant and the formulated one used in this work. There is evidence that this behavior can exist due to the role of the bonding agent, and the chemical mechanism discussed in details in Ref.[16]. A possible explanation for this behavior may be found by considering that at the first phase of aging (2 year aging) the oxidative cross-linking takes place which results from the free-radical attack at double bonds in the polymer chain backbone. However, the antioxidants are added to the propellant formulation to limit this effect. Also, the effect of the post-cure that appears in the first phase, due to some of the curing reactions, is slow and continues after fabrication. These two reactions result in

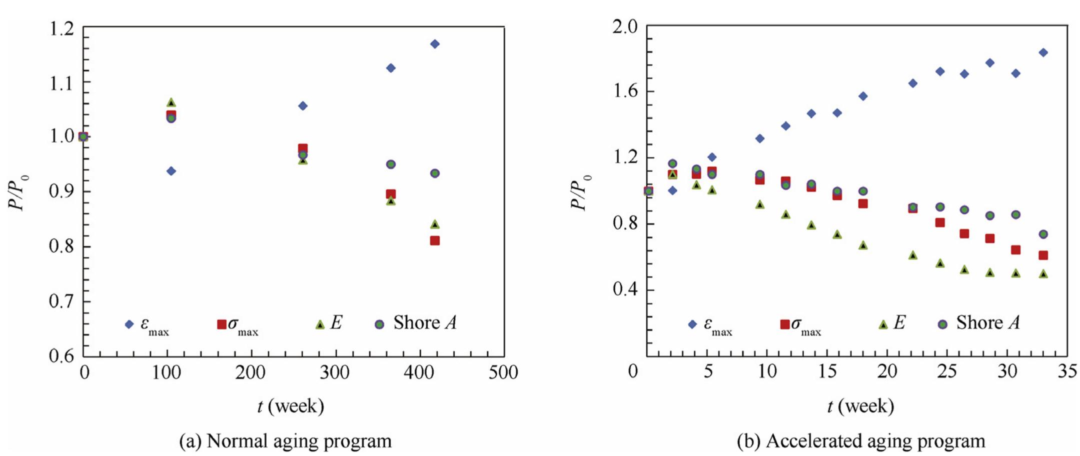

Fig. 4 Mechanical properties variation during normal and accelerated aging.

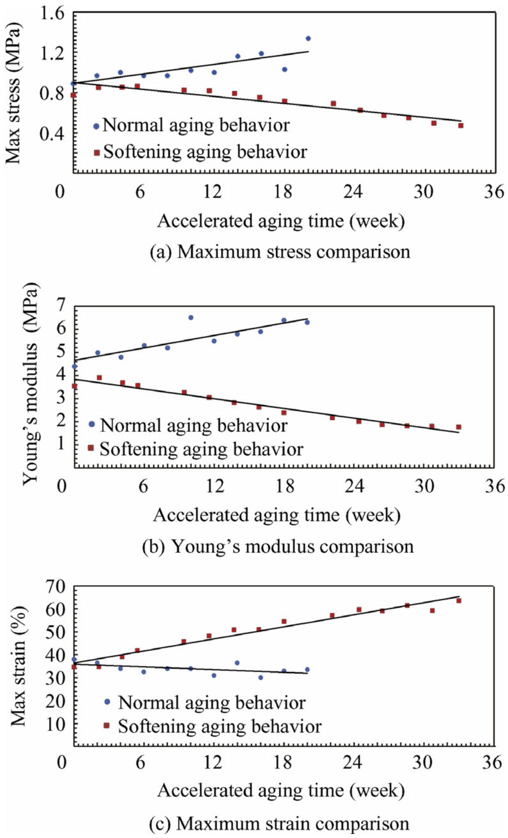

Fig. 5 Comparison of mechanical properties.

an increase in propellant stress and modulus followed by a decrease in the strain properties of solid propellant as shown in Fig. 3 for the curve of 2 year aging. The second phase (after 2 year aging) is chain scission and hydrolysis which result in softening of the propellant leading to a decrease of the stress and modulus and an increase ofthe strain as shown in Fig. 3 for the curves of 5, 7 and 8 years. The chain scission is determined by the cure system and undergoes aging due to the splitting of functional linkage if the binder itself of the cross-links generated during curing isweak enough. The hydrolysis occurs with polyesters where the ester links may catch hydrolysis due to the effect of moisture and lead to depolymerization of the binder.

3.2. Ballistic performance behavior

The results of the ballistic tests during the accelerated aging period at temperature 65 °C are listed in Table 3, and the variation of burning rate over the aging time is shown in Fig. 6.

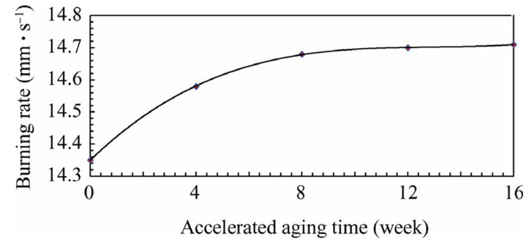

Fig. 6 Variation of burning rate with accelerated aging time.

From these results, it can be noticed that the maximum change in burning rate due to aging is small about 2.5%, and this percentage cannot affect the ballistic performance of the rocket motor as seen in other Refs.[3,27]

4. Aging kinetic modeling of propellant mechanical properties

In order to obtain a good mathematical kinetic model which can describe this complex aging behavior, the measuring data obtained from the uniaxial tensile tests of the aged composite solid propellant specimens were curve fitted as a function of time. In this investigation, linear, logarithmic, second-order polynomial, power law, and exponential functions were tried, and the best fit function for all aging mechanical properties in both conditions is an exponential equation with two terms as shown in Eq. (5).

$$P(t) = C_1\exp(k_1 t) + C_2\exp(k_2 t) \tag{5}$$

where C_1 and C_2 are the material constants, and the summation of these constants equals the value of the initial property at time zero ($C_1 + C_2 = P_0$). The proposed model consists of two different aging rate constants corresponding to the two main reactions which occur during the aging as shown in Fig. 7.

Both $k_1$and k_2 depend on temperature with individual activation energies and the combination of them will give the total constantrate, so the Arrhenius equation will be modified as shown in Eq. (6).

$$k = k_1 + k_2 = A_a\exp\left(\frac{-E_{ao}}{RT}\right) + A_h\exp\left(\frac{-E_{ah}}{RT}\right) \tag{6}$$

where A_a and A_h are the pre-exponential factors of the oxidation and hydrolysis reactions respectively, and E_{ao} and E_{ah} are two individual activation energy of the both reactions. Eq. (5) is applied to the mechanical property data and the output results of the aging rate constants are presented in Table 4.

The calculated rate constants for maximum stress and modulus increase as aging temperature increases while show inverse effect in propellant maximum strain. The values of the initial mechanical properties obtained from the mathematical model

Table 3 Ballistic characteristics of accelerated aged HTPB solid propellant.

Aging time (week)	Propellant weight (kg)	Burning time (s)	Average pressure (Bar)	Burning rate (mm·s^{-1})
0	0.373	2.111	64.04	14.35
4	0.372	2.101	63.98	14.58
8	0.374	2.033	63.91	14.68
12	0.374	2.026	63.90	14.70
16	0.372	2.041	63.94	14.71

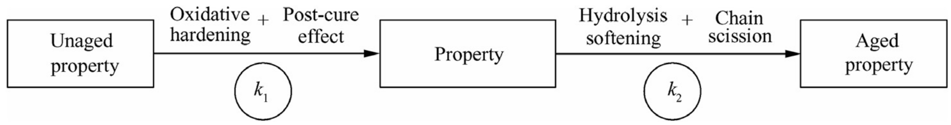

Fig. 7 Block diagram for mechanism of aging model.

Table 4 Fitting constants calculated for mechanical property changes during aging.

Mechanical property	Aging condition	Fitting constant						
		k_1	k_2	k	C_1	C_2	P_0	R^2
σ_{max} (σ_0 = 0.7737)	Normal aging	0.01869	0.0276	0.04629	3.892	−3.109	0.783	0.922
	Accelerated aging	0.02241	0.0374	0.26056	2.106	−1.308	0.798	0.951
ε_{max} (ε_0 = 34.66)	Normal aging	0.06415	0.1181	0.18225	21.02	13.62	34.64	0.997
	Accelerated aging	0.05655	0.0767	0.13325	64.62	−30.07	34.55	0.980
E (E_0 = 3.55)	Normal aging	0.03084	0.0482	0.0791	23.310	−19.75	3.56	0.986
	Accelerated aging	0.03540	0.5445	0.5799	3.987	-8.4×10^{-8}	3.98	0.965

(especially under normal aging condition) are very close to those obtained from the experimental test with a maximum deviation of 2%. The statistic value R^2 measures how successful the fit is in explaining the variation of the data, and in another way, it is the square of the correlation between the experimental values and the predicted response values. R^2 shows that the mathematical model has a good accuracy corresponding to the uniaxial tensile data.

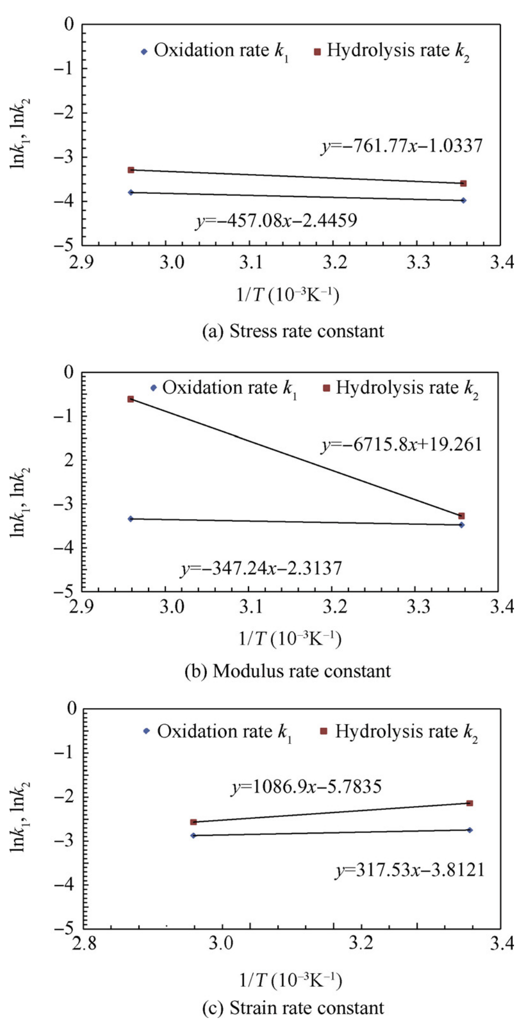

Fig. 8 Arrhenius curves for oxidative and hydrolysis rate constants.

Fig. 8 shows the Arrhenius curves for the oxidative hardening and hydrolysis rate constants calculated for stress, modulus, and strain respectively. Because of the rate, constant data appear to be linear, and therefore, the Arrhenius model can be used to describe the obtained aging mechanism. Using the values of the rate constants k which are listed in Table 4 at different temperatures, $\ln k_1$ and $\ln k_2$ versus $1/T$ graphs are formed as shown in Fig. 8, and then the Arrhenius parameters can be calculated as listed in Table 5.

The calculated activation energies E_a for stress, strain, and modulus consist of two parts relative to the oxidative hardening and hydrolysis rate constants, and the summation range between 10 and 60 kJ/mol, depending on the mechanical property considered. Generally, the activation energy of solid propellantvaries from 10 to 140 kJ/mol, and a lower value of the activation energy means that the degradation mechanism is diffusion controlled, while a higher value indicates kinetics controlled.[24] The negative activation energy seen in strain means that the reaction cannot be controlled and maybe cannot stop from occurring if we tried.

5. Service life prediction

Because the aging processes are mainly chemically caused, it is possible to use an empirical formula based on the generalized Van't Hoff rule[35,36] (see Eq. (7)) to find the corresponding real normal aging time, according to the accelerated aging time at different temperatures. Table 6 shows the relation between the normal and accelerated aging time.

$$t_E = \frac{t_T f^{\left(\frac{T_T - T_E}{\Delta T_F}\right)}}{365.25} \tag{7}$$

where t_E is the time in year at temperature T_E, t_T is the time in day at test temperature T_T, f is the reaction rate change factor per 10 °C temperature change f = 2.5, T_T is the test tempera-

Table 5 Arrhenius parameters.

Mechanical property	E_{ao} (kJ·mol^{-1})	E_{ah}(kJ·mol^{-1})	E_a(kJ·mol^{-1})	A_0	A_h
σ_{max}	3.80	6.33	10.13	0.086	0.355
ε_{max}	−2.63	−9.03	−11.66	0.022	0.003
E	2.88	55.83	58.71	0.098	231.7×10^6

Table 6 Correlation between normal and accelerated aging time.

Temperature (°C)	Aging condition	Time unit	Aging time							
25	Normal	year	2	5	8	10	13	15	20	25
65	Accelerated	day	20	45	75	95	120	140	190	235
		week	2.8	6.4	10.7	13.5	17.1	20	27.1	33.5

ture in °C, T_E is the in-service temperature in °C, and ΔT_F is the temperature interval for the actual value of f. Here ΔT_F is always 10 °C.

Service life prediction is dependent on the measure of the rate of change of critical material properties. From the results listed in Table 4 and the graphs of Arrhenius parameters shown in Fig. 8, it can be observed that the modulus E is the critical mechanical property in this study. Inspection reveals that E has the maximum rate of change during the aging period, and also has the maximum activation energy. Given the fact that the modulus is a function of both binder stiffness and binder/filler interactions, it is reasonable to assume that the modulus will be affected by anything in between.[16] Therefore, the degradation criterion is defined as the reduction of the modulus until it reaches to the minimum value specified by the designers for this type of propellant. From the accelerated aging experimental data, the propellant modulus is plotted versus the aging time in year as shown in Fig. 9, and then the proposed aging kinetic model (see Eq. (5)) is applied. Since Layton's empirical equation (see Eq. (1)) is the most common kinetic model used to describe the mechanical aging data, this model is applied to the modulus result. A comparison of the fitting results between the two models is shown in Fig. 9. It can be observed that the proposed aging model allowed a good fit to the experimental data, which was not possible by using Layton's model.

The minimum value of the modulus according to the propellant specifications is 2.55 MPa that means that the shelf life at normal temperature 25 °C is predicted for approximately 13 years. The corresponding shelf lifetime is 17 weeks with a consideration of the accelerated aging conditions at 65 °C, which is very near to the total accelerated aging time for the ballistic tests (16 weeks). So, the formulated solid propellant used in this study also satisfies the ballistic performance requirements, not only the mechanical one.

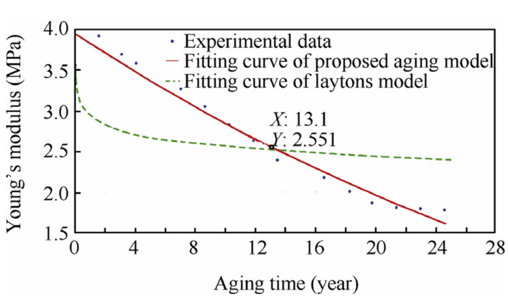

Fig. 9 Variation of Young's modulus with aging time.

6. Conclusions

(1) The mechanical properties of the solid propellant in the accelerated aging process represent the same trend and behavior of the normal aging process.
(2) The maximum tensile strength, Young's modulus, and Shore-hardness of HTPB propellant initially increase in the first stage of the aging due to the post-cure effect and the oxidative cross-linking bonds, and then in the second stage of the aging, the same properties start to decrease due to the chain degradation and the moisture hydrolysis.
(3) The mechanical properties are strongly affected by the temperature.
(4) The maximum strain initially decreases and then starts to increase with the increase of the aging time.
(5) The burning rate increases with the aging time, but by a very small value, about 2.5% of the initial value, this change cannot affect the ballistic performance of the rocket motor.
(6) The hydrolysis effect can be the main aging mechanism for AP/Al/HTPB propellant containing aziridine compounds as a bonding agent.
(7) The obtained kinetic model fits all mechanical properties of the aging propellant at normal and high temperatures.
(8) The results show that the squared correlation coefficients R^2 range from 0.922 to 0.997, which means that the fitting results of the proposed model have high accuracy.
(9) The kinetic model and Arrhenius equation are suitable for prediction of aging at normal storage temperature when the propellant softening is the major effect of aging.
(10) During the aging process, the modulus has the highest aging rate, which means that it will be dropped faster than any other mechanical property, so the propellant modulus is chosen as failure criteria of the present formulation.
(11) The shelf life predicted is determined to be about 13 years, and this time is safe, according to the mechanical and ballistic requirements for this solid propellant composition.

(12) Finally, the feasibility of the proposed aging life model can provide a reference for softening solid propellant mechanism and can be helpful for solid rocket motors' service life prediction.

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